

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 1 426 397 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

**09.06.2004 Bulletin 2004/24**(51) Int Cl.7: **C08G 73/10**(21) Application number: **03027011.0**(22) Date of filing: **22.11.2003**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR  
HU IE IT LI LU MC NL PT RO SE SI SK TR**

Designated Extension States:

**AL LT LV MK**(30) Priority: **05.12.2002 US 310313**

(71) Applicants:

- **Bayer Polymers LLC**  
**Pittsburgh, PA 15205 (US)**
- **Bayer Aktiengesellschaft**  
**51368 Leverkusen (DE)**

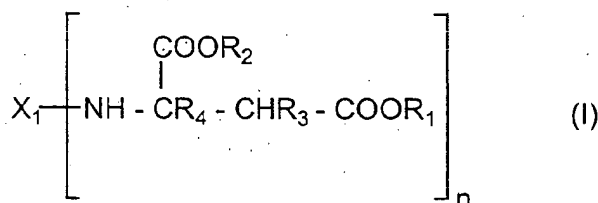
(72) Inventors:

- **Danielmeier, Karsten**  
**42659 Solingen-Burg (DE)**
- **Britsch, Catherine M.**  
**Pittsburgh PA 15212 (US)**

• **Gertzmann, Rolf****51377 Leverkusen (DE)**• **Vargo, Michele E.****Pittsburgh PA 15218 (US)**• **Wayt, Terrell D.****Moundsville WV 26041 (US)**• **Squiller, Edward P.****Bridgeville PA 15017 (US)**• **Roesler, Richard R.****Wexford PA 15090 (US)**(74) Representative: **Perchenek, Nils, Dr.****Bayer Aktiengesellschaft,****Bayer Polymers,****Law & Patents,****Patents and Licensing****51368 Leverkusen (DE)**(54) **Polyaspartate resins with good hardness and flexibility**

(57) The present invention relates to polyaspartate mixtures containing

a) 5 to 50 equiv.%, based on the total equivalents of aspartate groups, of a polyoxypropylene polyaspartate corresponding to the formula



wherein  $\text{X}_1$  represents the residue obtained by removing the amino groups from a polyoxypropylene polyamine having a functionality of  $n$ ,  $\text{R}_1$  and  $\text{R}_2$  are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of  $100^\circ\text{C}$  or less,  $\text{R}_3$  and  $\text{R}_4$  are identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at a temperature of  $100^\circ\text{C}$  or less and  $n$  is 2 to 4, and  
 b) 50 to 95 equiv.%, based on the total equivalents of aspartate groups, of a polyether polyaspartate corresponding to the formula I wherein  $\text{X}_1$  represents the residue obtained by removing the amino groups from a polyether polyamine having a functionality of  $n$  and a number average molecular weight of less than 5000, wherein the amino groups are attached to primary carbon atoms and the ether groups are separated by at least two carbon atoms.

The present invention also relates to a process for preparing these polyaspartate mixtures and to the polyureas prepared by reacting the polyaspartate mixtures and optionally other isocyanate-reactive compounds with polyisocyanates.

**Description**BACKGROUND OF THE INVENTIONField of the Invention

**[0001]** The present invention relates to polyaspartate mixtures prepared from a mixture of polyoxypropylene polyamines and low molecular weight polyether polyamines and to their use for the production of polyureas with good hardness and flexibility.

Description of the Prior Art

**[0002]** Two-component coating compositions containing a polyisocyanate component and a polyaspartate component are known and disclosed in U.S. Patents 5,126,170, 5,236,741, 5,489,704 and 5,516,873. The polyaspartates may be used as the only isocyanate-reactive component or they may be blended with polyols, polyamines or blocked polyamines, such as ketimines, aldimines or oxazolidines. The compositions are suitable for the preparation of high quality coatings that are abrasion resistant, solvent resistant and weather resistant.

**[0003]** One of the deficiencies of these polyaspartates is that when reacted with polyisocyanates they do not form coatings with a good combination of hardness and flexibility, which can be seen from the low hardnesses and elongations of the resulting coatings. One method for improving the flexibility is to prepare the polyaspartates from high molecular weight polyether polyamines, such as Jeffamine D-2000 (available from Huntsman). However, as disclosed in WO 01/07504, the reaction of equimolar amounts of this polyether polyamine with diethyl maleate to form the polyaspartate is only 78% complete after 73 days, and it takes more than 2 years for the reaction to be 100% complete.

**[0004]** Based on these teachings it would be expected that the preparation of a polyaspartate from a mixture of polyether polyamines would require an unacceptably long reaction time to achieve a complete or a substantially complete reaction.

**[0005]** Other alternatives for reducing the reaction time are also not feasible. For example, if a large excess of the ester of maleic or fumaric acid is used to reduce the reaction time, then it is necessary to remove the unreacted excess when the reaction is completed, which is a time-consuming, expensive procedure. It is also not feasible to prepare large quantities of the polyaspartates resins in advance because it is extremely difficult to predict customers' needs for the products and because of expensive storage and inventory costs.

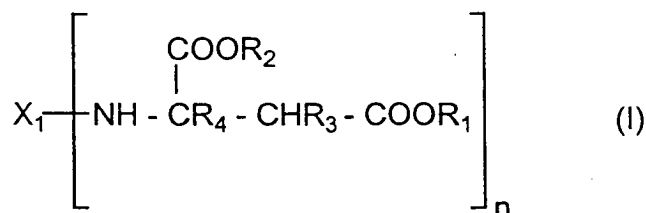
**[0006]** Accordingly, it is an object of the present invention to provide polyaspartate resins that can be reacted with polyisocyanates to obtain coatings with improved hardness and flexibility. It is an additional object of the present invention to provide polyaspartate resins that can be prepared with a short reaction time.

**[0007]** Surprisingly, these objects may be achieved with the polyaspartate resins according to the present invention which are prepared from a mixture of polyoxypropylene polyamines and low molecular weight polyether amines. When reacted with polyisocyanates the resulting coatings possess a good combination of hardness and flexibility. In addition, the polyaspartate resins can be prepared with a relatively short reaction time, which is surprising in view of the prior art which teaches that excessively long reaction times are required to prepare polyaspartates from polyether polyamines.

SUMMARY OF THE INVENTION

**[0008]** The present invention relates to polyaspartate mixtures containing

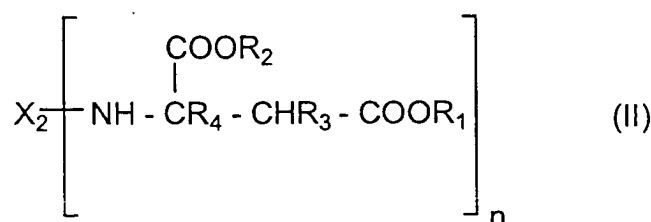
- a) 5 to 50 equiv.%, based on the total equivalents of aspartate groups, of a polyoxypropylene polyaspartate corresponding to the formula



wherein

$X_1$  represents the residue obtained by removing the amino groups from a polyoxypropylene polyamine having a functionality of  $n$ ,  
 $R_1$  and  $R_2$  are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of 100°C or less,  
 $R_3$  and  $R_4$  are identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at a temperature of 100°C or less and  
 $n$  is 2 to 4, and

b) 50 to 95 equiv.%, based on the total equivalents of aspartate groups, of a polyether polyaspartate corresponding to the formula



wherein

$X_2$  represents the residue obtained by removing the amino groups from a polyether polyamine having a functionality of  $n$  and a number average molecular weight of less than 5000, wherein the amino groups are attached to primary carbon atoms and the ether groups are separated by at least two carbon atoms.

**[0009]** The present invention also relates to a process for preparing these polyaspartate mixtures by

a) reacting one equivalent of unsaturated groups from maleic or fumaric acid esters corresponding to the formula



with 5 to 50 equiv.% of polyoxypropylene polyamines corresponding to the formula



to form a reaction mixture containing polyoxypropylene polyaspartates a) and excess maleic or fumaric acid esters (III) and

b) reacting the excess maleic or fumaric esters formula (III) with a substantially equivalent amount of a polyether polyamine corresponding to the formula



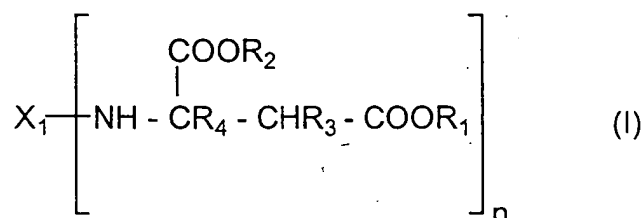
to form a mixture of polyoxypropylene polyaspartates a) and polyether polyaspartates b).

**[0010]** The present invention additionally relates to polyureas prepared by reacting the polyaspartate mixtures and optionally other isocyanate-reactive compounds with polyisocyanates.

## DETAILED DESCRIPTION OF THE INVENTION

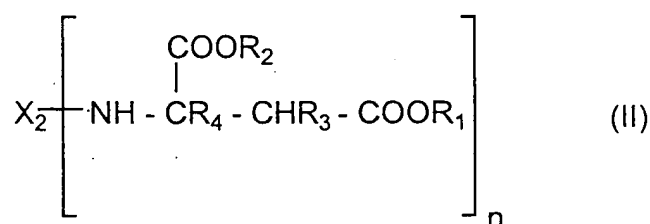
**[0011]** The polyaspartates according to the invention contain a mixture of 5 to 50 equiv.%, preferably 5 to 40 equiv.% and more preferably 5 to 20 equiv.% of polyoxypropylene polyaspartates a) and 50 to 95 equiv.%, preferably 60 to 95 equiv.% and more preferably 80 to 95 equiv.% of polyether polyaspartates b), wherein the preceding equiv.% are based on the total equivalents of aspartate groups.

**[0012]** Polyoxypropylene polyaspartates a) correspond to formula I



wherein

$\text{X}_1$  represents the residue obtained by removing the amino groups from a polyoxypropylene polyamine having a functionality of  $n$ . Polyether polyaspartates b) correspond to formula II



wherein

$\text{X}_2$  represents the residue obtained by removing the amino groups from a polyether polyamine having a functionality of  $n$  and a number average molecular weight of less than 5000, preferably less than 3000, more preferably less than 600, and most preferably less than 300, wherein the amino groups are attached to primary carbon atoms and the ether groups are separated by at least two carbon atoms.

**[0013]** In both formulas I and II

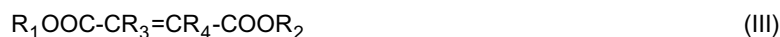
$\text{R}_1$  and  $\text{R}_2$  are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of 100°C or less, preferably alkyl groups having 1 to 9 carbon atoms, more preferably alkyl groups having 1 to 4 carbon atoms, such as methyl, ethyl or butyl groups,

$\text{R}_3$  and  $\text{R}_4$  may be identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at a temperature of 100°C or less, preferably hydrogen and

$n$  is 2 to 4, preferably 2 or 3 and more preferably 2.

**[0014]** With regard to the preceding definitions  $\text{R}_1$  and  $\text{R}_2$  may be different when the polyaspartates are prepared from mixed maleates, such as methylethyl maleate. In addition, one  $\text{R}_1$  may be different from another  $\text{R}_1$ . For example, when a mixture of maleates, e.g. dimethyl and diethyl maleate, is used to prepare the polyaspartate, one pair of  $\text{R}_1$  and  $\text{R}_2$  groups will be methyl and the other will be ethyl.

**[0015]** The polyaspartates may be prepared in accordance with known process conditions as described in U.S. Patent 5,126,170, herein incorporated by reference. According to a preferred embodiment of the present invention in the first step of the reaction one equivalent of maleic or fumaric acid esters corresponding to the formula



are reacted with 5 to 50 equiv.% of polyoxypropylene polyamines corresponding to the formula



to form polyoxypropylene polyaspartates a). The equiv.% of the polyoxypropylene polyamine is determined by dividing the equivalents of primary amino groups in the polyoxypropylene polyamine by the equivalents of unsaturated groups present in the maleic or fumaric acid esters of formula IV and multiplying the quotient by 100. The reaction may be carried out at a temperature of 0 to 100°C, preferably 20 to 65°C.

**[0016]** The reaction may be carried out solvent-free or in the presence of suitable solvents such as methanol, ethanol, propanol, dioxane, aromatic solvents such as toluene and mixtures of such solvents. Preferably, the reaction is carried out solvent-free. It is preferred to add the amine to the flask and then to add the maleic or fumaric acid ester such that the exothermic reaction is controllable. However, it is also possible to add the maleic or fumaric acid ester to the flask and slowly add the amine to the mixture. There is no need to use a catalyst, although one can be added to increase the reaction rate. Depending upon the temperature, the excess of unsaturated ester and the steric hindrance in the polyoxypropylene polyamine, the conversion of the polyoxypropylene polyamine to the polyoxypropylene polyaspartate a) is at least 98%, preferably 100%, complete in less than one week. By using a larger excess of the unsaturated ester, it is possible to reduce the reaction time to less 24 hours.

**[0017]** In the second step of the process the remaining equivalents of the unsaturated esters of formula III are reacted with a substantially equivalent amount of a polyether polyamine corresponding to the formula



This reaction conditions used in the first step are also suitable for use in the second step of the process. Excess starting materials and solvents, especially isocyanate-reactive solvents, may be removed by distillation after the reaction. The reaction is generally complete within four to six weeks after the reaction mixture is cooled to room temperature.

**[0018]** In accordance with another embodiment of the present invention polyoxypropylene polyaspartates a) and polyether polyaspartates b) are separately prepared and mixed in the desired ratios to form the polyaspartate mixtures. These mixtures can be used to prepare polyureas having good hardness and flexibility. However, when the polyaspartates are separately prepared the advantages of a faster reaction time will not be obtained. To obtain these improvements, it is necessary to prepare the polyaspartate mixtures in accordance with the preferred process previously set forth.

**[0019]** Suitable polyoxypropylene polyamines corresponding to formula IV are known can be prepared by methods such as those described in German Offenlegungsschrift No. 1,193,671, U.S. Pat. No. 3,236,895, French. Pat. No. 1,466,708, by the amination of polyoxypropylene polyols, which in turn are prepared by the alkoxylation of 1,2-propylene oxide. The polyoxypropylene polyamines preferably have a number average molecular weight of 200 to 5000, more preferably 1000 to 5000 and most preferably 1500 to 3000. Examples of polyoxypropylene diamines include Jeffamine D-2000 and Jeffamine D-230, both of which can be obtained from Huntsman Corporation. Examples of polyoxypropylene triamines include Jeffamine T-403, Jeffamine T-3000 and Jeffamine T-5000, which are also available from Huntsman.

**[0020]** Suitable polyether amines corresponding to formula V are those having linear or branched hydrocarbon chains interrupted by ether groups and having a number average molecular weight of less than 5000, preferably less than 3000, more preferably less than 600, and most preferably less than 300. The amino groups are attached to primary carbons and the ether groups are separated by at least two carbons. Preferably, the backbone of the polyether contains oxypropylene and/or oxyethylene groups.

**[0021]** Preferred polyamines are those corresponding to the formula



wherein

$R_5$  represents the residue obtained by removing the hydroxyl groups from a linear or branched hydrocarbon

radical having 2 to 10 carbon atoms, preferably 2 to 8 carbon atoms and more preferably 2 to 6 carbon atoms,

$R_6$  and  $R_7$  may be the same or different and represent linear or branched hydrocarbon radicals containing 2 to 8 carbon atoms, preferably 2 to 6 carbon atoms and more preferably 2 to 4 carbon atoms and

$x$  has a value of 1 to 70, preferably 1 to 45, more preferably 1 to 10 and most preferably 1 to 5.

**[0022]** Examples include 2-[2-(2-aminoethoxy)ethoxy]ethylamine (Jeffamine XTJ-504, available from Huntsman), 3-[2-(3-aminopropoxy)ethoxy]propylamine (Etheramine NDPA 10, available from Tomah Products), 3-[3-(3-aminopropoxy)propoxy]propylamine (Etheramine NDPA 11, available from Tomah Products), 3-[4-(3-amino-propoxy)butoxy]propylamine (Etheramine NDPA 12, available from Tomah Products) and 3-[2-[2-(3-aminopropoxy)ethoxy]ethoxy]propylamine (Etheramine DPA-DEG, available from Tomah Products or BASF TTD, available from BASF).

**[0023]** Examples of suitable maleic or fumaric acid esters corresponding to formula III include dimethyl, diethyl and dibutyl (e.g., di-n-butyl), diamyl, di-2-ethylhexyl esters and mixed esters based on mixtures of these and/or other alkyl groups of maleic acid and fumaric acid; and the corresponding maleic or fumaric acid esters substituted by methyl in the 2- and/or 3-position. The dimethyl, diethyl and dibutyl esters of maleic acid are preferred, while the diethyl esters are especially preferred.

**[0024]** The polyaspartate mixtures according to the invention may be combined with polyisocyanates to form two-component compositions that are suitable for the preparation of polyurea coatings, sealants and adhesives. The polyaspartate mixtures may be used as the only isocyanate-reactive component or they may be blended with other isocyanate-reactive components, such as polyols. In accordance with the present invention polyureas include polymers containing urea groups and optionally urethane groups. The polyaspartate mixtures may also be blended with compounds containing amine-reactive groups, such as epoxy groups, carbonate groups and lactones, and reacted to form the corresponding polymers.

**[0025]** Suitable polyisocyanates for preparing the polyureas include monomeric polyisocyanates, polyisocyanate adducts and NCO prepolymers, preferably monomeric polyisocyanates and polyisocyanate adducts. The polyisocyanates have an average functionality of 1.8 to 8, preferably 2 to 6 and more preferably 2 to 5.

**[0026]** Suitable monomeric diisocyanates include those represented by the formula



in which R represents an organic group obtained by removing the isocyanate groups from an organic diisocyanate having a molecular weight of about 112 to 1,000, preferably about 140 to 400. Preferred diisocyanates are those in which R represents a divalent aliphatic hydrocarbon group having 4 to 40, preferably 4 to 18 carbon atoms, a divalent cycloaliphatic hydrocarbon group having 5 to 15 carbon atoms, a divalent araliphatic hydrocarbon group having 7 to 15 carbon atoms or a divalent aromatic hydrocarbon group having 6 to 15 carbon atoms.

**[0027]** Examples of the suitable organic diisocyanates include 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (isophorone diisocyanate or IPDI), bis-(4-iso-cyanatocyclohexyl)-methane, 2,4'-dicyclohexyl-methane diisocyanate, 1,3- and 1,4-bis-(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methyl-cyclohexyl)-methane,  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and/or -1,4-xylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 2,4- and/or 2,6-hexahydrotolylene diisocyanate, 1,3- and/or 1,4-phenylene diisocyanate, 2,4- and/or 2,6-tolylene diisocyanate, 2,4-and/or 4,4'-diphenyl-methane diisocyanate, 1,5-diisocyanato naphthalene and mixtures thereof.

**[0028]** Polyisocyanates containing 3 or more isocyanate groups such as 4-isocyanatomethyl-1,8-octamethylene diisocyanate and aromatic polyisocyanates such as 4,4',4''-triphenylmethane triisocyanate and polyphenyl polymethylene polyisocyanates obtained by phosgenating aniline/formaldehyde condensates may also be used.

**[0029]** Preferred organic diisocyanates include 1,6-hexamethylene diisocyanate, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanatocyclohexyl)-methane, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 2,4- and/or 2,6-tolylene diisocyanate, and 2,4- and/or 4,4'-diphenyl-methane diisocyanate.

**[0030]** Suitable polyisocyanate adducts include those prepared from the preceding monomeric polyisocyanates and containing isocyanurate, uretdione, biuret, urethane, allophanate, iminooxadiazine dione, carbodiimide, acylurea and/or oxadiazinetrione groups. The polyisocyanates adducts, which preferably have an NCO content of 5 to 30% by weight, include:

1) Isocyanurate group-containing polyisocyanates which may be prepared as set forth in DE-PS 2,616,416, EP-OS 3,765, EP-OS 10,589, EP-OS 47,452, US-PS 4,288,586 and US-PS 4,324,879. The isocyanato-isocyanurates generally have an average NCO functionality of 3 to 4.5 and an NCO content of 5 to 30%, preferably 10 to 25% and most preferably 15 to 25% by weight.

2) Uretidione diisocyanates which may be prepared by oligomerizing a portion of the isocyanate groups of a diisocyanate in the presence of a suitable catalyst, e.g., a trialkyl phosphine catalyst, and which may be used in admixture with other aliphatic and/or cycloaliphatic polyisocyanates, particularly the isocyanurate group-containing polyisocyanates set forth under (1) above.

3) Biuret group-containing polyisocyanates which may be prepared according to the processes disclosed in U.S. Patent Nos. 3,124,605; 3,358,010; 3,644,490; 3,862,973; 3,906,126; 3,903,127; 4,051,165; 4,147,714; or 4,220,749 by using co-reactants such as water, tertiary alcohols, primary and secondary monoamines, and primary and/or secondary diamines. These polyisocyanates preferably have an NCO content of 18 to 22% by weight.

4) Urethane group-containing polyisocyanates which may be prepared in accordance with the process disclosed in U.S. Patent No. 3,183,112 by reacting excess quantities of polyisocyanates, preferably diisocyanates, with low molecular weight glycols and polyols having molecular weights of less than 400, such as trimethylol propane, glycerine, 1,2-dihydroxy propane and mixtures thereof. The urethane group-containing polyisocyanates have a most preferred NCO content of 12 to 20% by weight and an (average) NCO functionality of 2.5 to 3.

5) Allophanate group-containing polyisocyanates which may be prepared according to the processes disclosed in U.S. Patent Nos. 3,769,318, 4,160,080 and 4,177,342. The allophanate group-containing polyisocyanates have a most preferred NCO content of 12 to 21 % by weight.

6) Isocyanurate and allophanate group-containing polyisocyanates which may be prepared in accordance with the processes set forth in U.S. Patents 5,124,427, 5,208,334 and 5,235,018, the disclosures of which are herein incorporated by reference, preferably polyisocyanates containing these groups in a ratio of monoisocyanurate groups to mono-allophanate groups of about 10:1 to 1:10, preferably about 5:1 to 1:7.

7) Iminooxadiazine dione and optionally isocyanurate group-containing polyisocyanates which may be prepared in the presence of special fluorine-containing catalysts as described in DE-A 19611849. These polyisocyanates generally have an average NCO functionality of 3 to 3.5 and an NCO content of 5 to 30%, preferably 10 to 25% and most preferably 15 to 25% by weight.

8) Carbodiimide group-containing polyisocyanates which may be prepared by oligomerizing di- or polyisocyanates in the presence of known carbodiimidization catalysts as described in DE-PS 1,092,007, US-PS 3,152,162 and DE-OS 2,504,400, 2,537,685 and 2,552,350.

9) Polyisocyanate containing acylurea groups, which may be prepared by the direct reaction of isocyanates with carboxylic acids or via a carbodiimide intermediate stage as described, e.g., in A.H.M. Schotman et.al. Recl. Trav. Chim. Pay-Basm 1992, 111, 88-91, P. Babusiaux et al., Liebigs Ann. Chem. 1976, 487-495, German Auslegeschrift 1 230 778, DE-A 2 436 740 and the literature cited therein.

10) Polyisocyanates containing oxadiazinetriene groups and containing the reaction product of two moles of a diisocyanate and one mole of carbon dioxide.

**[0031]** Preferred polyisocyanate adducts are the polyisocyanates containing isocyanurate, uretidione, biuret, iminooxadiazine dione and/or allophanate groups.

**[0032]** The NCO prepolymers, which may also be used to prepare the polyureas according to the invention are prepared from the previously described monomeric polyisocyanates or polyisocyanate adducts, preferably monomeric diisocyanates, and polyhydroxyl compounds containing at least two hydroxyl groups. These polyhydroxyl compounds include high molecular weight compounds having molecular weights of 500 to about 10,000, preferably 800 to about 8,000, and more preferably 1800 to 8,000, and optionally low molecular weight compounds having molecular weights of less than 500. The molecular weights are number average molecular weights ( $M_n$ ) and are determined by end group analysis (OH number). Products obtained by reacting polyisocyanates exclusively with low molecular weight compounds are polyisocyanates adducts containing urethane groups and are not considered to be NCO prepolymers.

**[0033]** Examples of the high molecular weight compounds are polyester polyols, polyether polyols, polyhydroxy polycarbonates, polyhydroxy polyacetals, polyhydroxy polyacrylates, polyhydroxy polyester amides and polyhydroxy polythioethers. The polyether polyols, polyester polyols and polycarbonate polyols are preferred. Examples of the high molecular weight and low molecular weight polyhydroxy compounds are disclosed in U.S. Patent 4,701,480, herein incorporated by reference.

**[0034]** These NCO prepolymers preferably have an isocyanate content of 0.3 to 35% by weight, more preferably 0.6 to 25% by weight and most preferably 1.2 to 20% by weight. The NCO prepolymers are produced by reacting the diisocyanates with the polyol component at a temperature of 40 to 120°C, preferably 50 to 100°C, at an NCO/OH equivalent ratio of 1.3:1 to 20:1, preferably 1.4:1 to 10:1. If chain extension via urethane groups is desired during the preparation of the isocyanate prepolymers, an NCO/OH equivalent ratio of 1.3:1 to 2:1 is selected. If chain extension

is not desired, an excess of diisocyanate is preferably used, corresponding to an NCO/OH equivalent ratio of 4:1 to 20:1, preferably 5:1 to 10:1. The excess diisocyanate may optionally be removed by thin layer distillation when the reaction is completed. In accordance with the present invention NCO prepolymers also include NCO semi-prepolymers which contain unreacted starting polyisocyanates in addition to the urethane group-containing prepolymers.

**[0035]** Suitable compounds that may optionally be used in combination with the polyaspartate mixtures as the isocyanate-reactive component for preparing the two-component compositions include the known isocyanate-reactive compounds from polyurethane or polyurea chemistry. Examples include the high and low molecular weight, polyols previously disclosed for preparing the NCO prepolymers. Also suitable are the known high molecular weight amine-functional compounds, which may be prepared by converting the terminal hydroxy groups of the polyols previously described to amino groups, and the polyaldimines disclosed in U.S. Patent No. 5,466,771, herein incorporated by reference. The high molecular weight polyols are preferred.

**[0036]** The two-component coating compositions of the present invention may be prepared by mixing the individual components. It is preferred to mix the isocyanate-reactive components together and then to blend the resulting mixture with the polyisocyanate component. The polyisocyanate component and isocyanate-reactive component are present in an amount sufficient to provide an equivalent ratio of isocyanate groups is isocyanate-reactive of 0.5:1 to 2:1, preferably 0.9:1 to 1.5:1, more preferably 0.9:1 to 1.3:1 and most preferably 1:1 to 1.2:1.

**[0037]** Preparation of the compositions may be carried out solvent-free or in the presence of the solvents conventionally used in polyurethane or polyurea chemistry. It is an advantage of the present invention that the quantity of solvent used may be greatly reduced when compared with that required in conventional two-component compositions based on polyisocyanates and polyols.

**[0038]** Examples of suitable solvents include xylene, butyl acetate, methyl isobutyl ketone, methoxypropyl acetate, N-methyl pyrrolidone, Solvesso solvent, petroleum hydrocarbons and mixtures of such solvents.

**[0039]** In the coating compositions to be used for the process according to the invention, the ratio by weight of the total quantity of reactive components to the quantity of solvent is about 40:60 to 100:0, preferably about 60:40 to 100:0.

**[0040]** In addition to the reactive components, the coating compositions may also contain the known additives from coatings technology, such as fillers, pigments, softeners, high-boiling liquids, catalysts, UV stabilizers, anti-oxidants, microbiocides, algicides, dehydrators, thixotropic agents, wetting agents, flow enhancers, matting agents, anti-slip agents, aerators and extenders.

**[0041]** The two-component compositions according to the invention have relatively fast dry times. The resulting polyureas are flexible, have good chemical and weather resistance, and also have a high gloss and good pigmenting qualities.

**[0042]** The reaction to form the urea groups is carried out at a temperature of 10 to 100°C, preferably 20 to 80°C and more preferably 20 to 50°C. In accordance with the present invention the urea groups initially formed may be converted to hydantoin groups in known manner, e.g., by heating the compounds at elevated temperatures, optionally in the presence of a catalyst. Hydantoin groups will also form over time under ambient conditions. Therefore, the term "urea groups" is also intended to include other compounds containing the group, N-CO-N, such as hydantoin groups.

**[0043]** The invention is further illustrated, but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified.

## EXAMPLES

Polyaspartate 1 - Preparation of a polyaspartate mixture from a 2000 MW polyoxypropylene diamine and 3-[2-(3-aminopropoxy)ethoxy propylamine

**[0044]** A round bottom flask was fitted with stirrer, heating mantle, nitrogen inlet, thermocouple and addition funnel. 59.5 g (0.061 eq.) of a polyoxypropylene diamine (Jeffamine D 2000, available from Huntsman) were admitted to the flask at room temperature. 129.9 g (0.727 eq) of diethyl maleate were admitted through the addition funnel over a period of sixty minutes. The temperature of the flask was held at 35°C. The reaction mixture was heated to 60°C and held for 5 hours until the unsaturation number indicated that the conversion to aspartate was complete. Then 60.6 g (0.667 eq) of 3-[2-(3-aminopropoxy)ethoxy propylamine (NDPA-1 0, available from Tomah Products) were added. The temperature was held at 60°C for 12 hours and then cooled to RT. An iodometric titration showed that the reaction was complete in less than four weeks at room temperature. The clear, colorless final product had an amine number of 162.9 (theoretical amine number: 163.4 a viscosity of 180 cps@25°C and a density of 8.82 lbs/gal.

Polyaspartate 2 (Comparison) - Polyaspartate from a 2000 MW polyoxypropylene diamine

**[0045]** A round bottom flask was fitted with a stirrer, heating mantle, nitrogen inlet, thermocouple and addition funnel. 213.29 g (0.213 eq.) of a polyoxypropylene diamine (Jeffamine D 2000, available from Huntsman) were admitted to



## EP 1 426 397 A1

the flask at room temperature. 36.71 g (0.213 eq) of diethyl maleate were admitted through the addition funnel over a period of sixty minutes. The temperature of the flask was held at 35°C. The reaction mixture was heated to 60°C, held for 12 hours at that temperature and then cooled to room temperature. An iodometric titration showed that the reaction was not complete after 6 months at room temperature. The clear, colorless final product had an amine number of 46 (theoretical amine number: 47.8).

### Polyaspartate 3 (Comparison)

**[0046]** A polyaspartate prepared from bis-(4-aminocyclohexyl)-methane (Desmophen NH 1420, available from Bayer).

### Polyaspartate 4 (Comparison)

**[0047]** A polyaspartate prepared from 2-methyl-1,5-pentane diamine (Desmophen NH 1220, available from Bayer).

### Polyisocyanate 1

**[0048]** An isocyanurate group-containing polyisocyanate prepared from 1,6-hexamethylene diisocyanate and having an isocyanate content of 21.6%, a content of monomeric diisocyanate of <0.2% and a viscosity at 20°C of 3000 mPa.s (available from Bayer Corporation as Desmodur N 3300).

### Application Examples

**[0049]** Polyaspartates 1-4 were hand mixed with polyisocyanate 1 at an NCO:NH equivalent ratio of 1. Viscosity was measured on a Brookfield Viscometer. Pot life is the time from when the two components were mixed until the time when the mixture solidified.

**[0050]** The dry times of films prepared from the compositions were measured by doing a drawdown of the compositions on glass at a 10 mil wet film thickness. At 2-minute intervals, a cotton ball was pressed on the drawdown to test for film cure. The film was completely cured when the cotton ball did not leave an imprint. Tensile strength and % elongation were determined on an Instron 4444 machine according to ASTM D412. Shore D Hardness was measured by pouring the compositions into aluminum cups (thickness: 0.75 cm) and testing for hardness after curing for 3 days with a Shore Durometer Type D-2, ASTM D2240.

Example No.	Aspartate	Aspartate rxn time	Dry-time	Potlife	Shore D hard-ness	Tensile Strength psi	% Elong-ation
Example 1	1	<2 weeks	2-3 min	<30 sec	20	1125	147
Comparison Example 2	2	>6 months	>1.5 h	>1,5 h	Shore A 15	110	40
Comparison Example 3	3	>6 months	30 min	20 min	78	7493	2
Comparison Example 4	4	<2 weeks	<2 min	1 min	77	8115	2

**[0051]** Example 1 clearly demonstrates a good combination of hardness and elongation (the latter is an indicator for

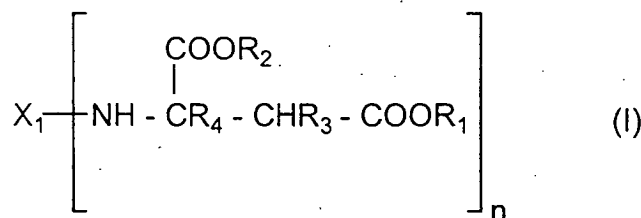
flexibility) when compared to Comparison Examples 2-4. Even though the hardness for Example 1 is slightly less than in Comparison Examples 3 and 4, the elongation is substantially improved. Comparison Examples 3 and 4 were based on commercially available polyaspartates and resulted in hard, inflexible coatings. Comparison Example 2 demonstrates that high molecular weight polyether diamines also provide increased flexibility versus Comparison Examples 3 and 4, but the coatings are very soft, the synthesis time is unacceptably long and the flexibility is less than in Example 1. This latter finding must be regarded as surprising since it would be expected that the flexibility would be higher for polyaspartate 2 due to the higher molecular weight of the diamine starting material.

**[0052]** Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

## Claims

1. A polyaspartate mixture comprising

a) 5 to 50 equiv.%, based on the total equivalents of aspartate groups, of a polyoxypropylene polyaspartate corresponding to the formula



wherein

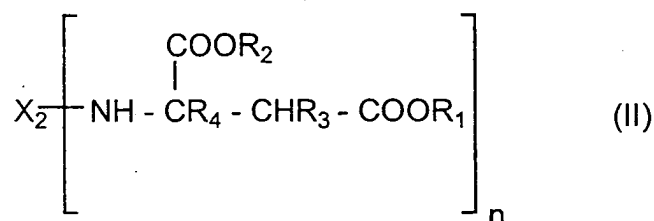
$\text{X}_1$  represents the residue obtained by removing the amino groups from a polyoxypropylene polyamine having a functionality of  $n$ ,

$\text{R}_1$  and  $\text{R}_2$  are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of 100°C or less,

$\text{R}_3$  and  $\text{R}_4$  are identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at a temperature of 100°C or less and

$n$  is 2 to 4, and

b) 50 to 95 equiv.%, based on the total equivalents of aspartate groups, of a polyether polyaspartate corresponding to the formula



wherein

$\text{X}_2$  represents the residue obtained by removing the amino groups from a polyether polyamine having a functionality of  $n$  and a number average molecular weight of less than 5000, wherein the amino groups are attached to primary carbon atoms and the ether groups are separated by at least two carbon atoms.

2. The polyaspartate of Claim 1 wherein

$X_2$  represents the residue obtained by removing the amino groups from a polyether polyamine having a number average molecular weight of less than 600 and corresponding to the formula



wherein

$R_5$  represents the residue obtained by removing the hydroxyl groups from a linear or branched hydrocarbon radical having 2 to 10 carbon atoms,

$R_6$  and  $R_7$  may be the same or different and represent linear or branched hydrocarbon radicals containing 2 to 8 carbon atoms and

$x$  has a value of 1 to 10.

3. The polyaspartate of Claim 2 wherein

$R_5$  represents the residue obtained by removing the hydroxyl groups from a linear or branched hydrocarbon radical having 2 to 6 carbon atoms,

$R_6$  and  $R_7$  may be the same or different and represent linear or branched hydrocarbon radicals containing 2 to 4 carbon atoms and

$x$  has a value of 1 to 5.

4. The polyaspartate of Claim 2 wherein polyoxypolypropylene polyaspartate a) is present in an amount of 5 to 40 equiv. %, based on the total equivalents of aspartate groups, and polyether polyaspartate b) is present in an amount of 60 to 95 equiv.%, based on the total equivalents of aspartate groups.

5. The polyaspartate of Claim 1 wherein

$R_1$  and  $R_2$  are identical or different and represent alkyl groups having 1 to 9 carbon atoms and  $R_3$  and  $R_4$  represent hydrogen.

6. The polyaspartate of Claim 2 wherein

$R_1$  and  $R_2$  are identical or different and represent alkyl groups having 1 to 9 carbon atoms and  $R_3$  and  $R_4$  represent hydrogen.

7. The polyaspartate of Claim 3 wherein

$R_1$  and  $R_2$  are identical or different and represent alkyl groups having 1 to 9 carbon atoms and  $R_3$  and  $R_4$  represent hydrogen.

8. The polyaspartate of Claim 4 wherein

$R_1$  and  $R_2$  are identical or different and represent alkyl groups having 1 to 9 carbon atoms and  $R_3$  and  $R_4$  represent hydrogen.

9. The polyaspartate of Claim 1 wherein

$R_1$  and  $R_2$  are identical or different and represent alkyl groups having 1 to 4 carbon atoms,  $R_3$  and  $R_4$  represent hydrogen and  $n$  is 2.

10. The polyaspartate of Claim 2 wherein

$R_1$  and  $R_2$  are identical or different and represent alkyl groups having 1 to 4 carbon atoms,  
 $R_3$  and  $R_4$  represent hydrogen and  
 $n$  is 2.

11. The polyaspartate of Claim 3 wherein

$R_1$  and  $R_2$  are identical or different and represent alkyl groups having 1 to 4 carbon atoms,  
 $R_3$  and  $R_4$  represent hydrogen and  
 $n$  is 2.

12. The polyaspartate of Claim 4 wherein

$R_1$  and  $R_2$  are identical or different and represent alkyl groups having 1 to 4 carbon atoms,  
 $R_3$  and  $R_4$  represent hydrogen and  
 $n$  is 2.

13. The polyaspartate of Claim 10 wherein

X represents the residue obtained by removing the amino groups from 3-[2-(3-aminopropoxy) ethoxy]propylamine.

14. The polyaspartate of Claim 12 wherein

X represents the residue obtained by removing the amino groups from 3-[2-(3-aminopropoxy)ethoxy]propylamine.

15. A process for preparing the polyaspartate mixture of Claim 1 which comprises

a) reacting one equivalent of unsaturated groups from a maleic or fumaric acid ester corresponding to the formula

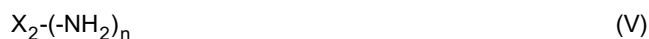


with 5 to 50 equiv.% of a polyoxypropylene polyamine corresponding to the formula



to form a reaction mixture containing a polyoxypropylene polyaspartate a) and excess maleic or fumaric acid ester (III) and

b) reacting the excess maleic or fumaric ester (III) with a substantially equivalent amount of a polyether polyamine corresponding to the formula



to form a mixture of polyoxypropylene polyaspartate a) and polyether polyaspartate b).

16. The process of Claim 15 wherein

$X_2$  represents the residue obtained by removing the amino groups from a polyether polyamine corresponding to the formula



wherein

$\text{R}_5$  represents the residue obtained by removing the hydroxyl groups from a linear or branched hydrocarbon radical having 2 to 10 carbon atoms,  
 $\text{R}_6$  and  $\text{R}_7$  may be the same or different and represent linear or branched hydrocarbon radicals containing 2 to 8 carbon atoms and  
 $x$  has a value of 1 to 10.

17. The process of Claim 15 wherein

$\text{R}_1$  and  $\text{R}_2$  are identical or different and represent alkyl groups having 1 to 4 carbon atoms,

$\text{R}_3$  and  $\text{R}_4$  represent hydrogen and

$n$  is 2.

18. The process of Claim 16 wherein

$\text{R}_1$  and  $\text{R}_2$  are identical or different and represent alkyl groups having 1 to 4 carbon atoms,

$\text{R}_3$  and  $\text{R}_4$  represent hydrogen and

$n$  is 2.

19. A polyurea which comprises the reaction product of a polyisocyanate with an isocyanate-reactive component comprising the polyaspartate mixture of Claim 1.

20. The polyurea of Claim 19 wherein the isocyanate-reactive component additionally contains a polyol.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 03 02 7011

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X,D	WO 01 07504 A (ROESLER RICHARD R ;BAYER AG (US)) 1 February 2001 (2001-02-01) * page 3, line 15 - page 4, line 9 * * page 7, line 3 - page 7, line 10 * * claims 1,6,10 *	1-14	C08G73/10
A	WO 01 07399 A (ROESLER RICHARD R ;BAYER AG (US)) 1 February 2001 (2001-02-01) * page 3, line 13 - page 4, line 7 * * claims 1-3 *	1-20	
A	EP 1 038 897 A (AIR PROD & CHEM) 27 September 2000 (2000-09-27) * paragraphs [0022]-[0024] * * claims 1,5-7 *	1-20	
A	EP 0 849 301 A (BAYER AG) 24 June 1998 (1998-06-24) * page 5, line 28 - page 6, line 16 * * page 6, line 34 - page 6, line 44 * * page 7, line 55 - page 8, line 5 * * claims 1,7-9 *	1-20	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08G
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 20 February 2004	Examiner Heidenhain, R
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 02 7011

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-02-2004

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 0107504	A	01-02-2001	AT	251195 T	15-10-2003
			AU	6226800 A	13-02-2001
			CA	2380271 A1	01-02-2001
			DE	60005698 D1	06-11-2003
			EP	1208135 A1	29-05-2002
			WO	0107504 A1	01-02-2001
			US	6590066 B1	08-07-2003
-----					
WO 0107399	A	01-02-2001	AT	253550 T	15-11-2003
			AU	6231000 A	13-02-2001
			BR	0012700 A	09-04-2002
			CA	2379967 A1	01-02-2001
			CN	1362946 T	07-08-2002
			DE	60006403 D1	11-12-2003
			EP	1210319 A1	05-06-2002
			JP	2003505555 T	12-02-2003
			WO	0107399 A1	01-02-2001
-----					
EP 1038897	A	27-09-2000	CN	1267694 A	27-09-2000
			EP	1038897 A2	27-09-2000
			JP	2000309746 A	07-11-2000
-----					
EP 0849301	A	24-06-1998	US	5736604 A	07-04-1998
			AT	253606 T	15-11-2003
			CA	2222481 A1	17-06-1998
			DE	69725956 D1	11-12-2003
			EP	0849301 A1	24-06-1998
			JP	10176138 A	30-06-1998
-----					

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82